

An experimental measurement of the staggered magnetization curve for a Haldane spin chain.

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(February 1, 2008)

Long-range magnetic ordering in $R_2\text{BaNiO}_5$ (R =magnetic rare earth) quasi-1-dimensional mixed-spin antiferromagnets is described by a simple mean-field model that is based on the intrinsic staggered magnetization function of isolated Haldane spin chains for the Ni-subsystem, and single-ion magnetization functions for the rare earth ions. The model is applied to new experimental results obtained in powder diffraction experiments on $\text{Nd}_2\text{BaNiO}_5$ and NdYBaNiO_5 , and to previously published diffraction data for $\text{Er}_2\text{BaNiO}_5$. From this analysis we extract the bare staggered magnetization curve for Haldane spin chains in these compounds.

75.25.+z, 75.10.-b, 75.10.Jm, 75.50.Ee

The quantum-disordered ground state and the famous Haldane energy gap in the magnetic excitation spectrum [1] have kept one-dimensional (1-D) integer-spin Heisenberg antiferromagnets (HAF) at the center of attention of condensed matter physicists for the last 15 years. Among the more recent developments are studies of such systems in external uniform magnetic fields [2–4]. It was found that in sufficiently strong fields one of the three Haldane-gap modes undergoes a complete softening at some particular wave vector. The result is a transition to a new phase with long-range antiferromagnetic correlations (see for example Refs. [5,6]). The effect of a *staggered* field \mathbf{H}_π , to which a Haldane chain is most susceptible, is expected to be no less dramatic. Unfortunately, this problem has been given much less attention in literature, simply because such conditions are almost impossible to realize in an experiment. The only chance of producing a magnetic field modulated on the *microscopic* scale is to make use of some periodic modulation that is intrinsic to the system under investigation. This can be, for example, a structural modulation, as is the case in NENP, one of the best-known Haldane-gap compounds (Refs. [7,8] and references therein). The $S = 1$ chains in this material consist of alternating crystallographically non-equivalent Ni^{2+} ions with slightly different gyromagnetic ratios. A weak effective staggered field can thus be induced in NENP by applying a *uniform* external field [9]. Unfortunately, the effect of the staggered component is obscured by the response of the system to the strong uniform field itself [9,10].

A more direct approach is to use an intrinsic *magnetic*

modulation in a material that, in addition to integer-spin Heisenberg chains, has other magnetic ions. Should the latter become ordered magnetically with an appropriate propagation vector, they will project an effective staggered exchange field on the Haldane spin chains. The magnitude of the staggered field can be varied in an experiment indirectly, by changing the temperature, and thus the magnitude of the magnetic order parameter. By measuring the induced moment on the Haldane chains one can hope to directly measure the *staggered magnetization curve for a Haldane spin system*. This function, that we shall denote as $\mathcal{M}(H_\pi)$, is one of the principal characteristics of a quantum-disordered integer-spin HAF, but to date has not been determined experimentally. In the present paper we shall demonstrate how $\mathcal{M}(H_\pi)$ can be determined by properly analyzing the results of simple neutron diffraction experiments.

It appears that the best experimental realizations of the mechanism described in the previous paragraph are to be found among linear-chain nickelates with the general formula $R_2\text{BaNiO}_5$ (R =magnetic rare earth). The $S = 1$ Ni^{2+} ions in these compounds are arranged in distinct chains that run along the a axis of the orthorhombic crystal structure. In-chain interactions between the Ni spins are antiferromagnetic, with the exchange constant $J \approx 300$ K, and interchain coupling is negligible. The magnetic R^{3+} ions are positioned in between the Ni chains, and are expected to be weakly coupled to the Ni^{2+} moments (exchange parameters of the order of tens of Kelvin) and even weaker between themselves (coupling constants of less than 1 K) [11]. All $R_2\text{BaNiO}_5$ species order antiferromagnetically with Néel temperatures ranging from 16 to 80 K [11,12]. In the ordered phase a non-zero ordered moment is found on both R^{3+} and Ni^{2+} sites. The magnetic order parameter of Ni^{2+} never achieves complete saturation, and at $T \rightarrow 0$ is substantially smaller than the expected value of $2\mu_B$ per ion, a hint at that quantum spin fluctuations in the Ni-chains survive well below the Néel temperature T_N . Haldane gap excitations propagating on the $S = 1$ Ni-chains have been observed both above and below the Néel temperature in all materials studied so far, including $\text{Pr}_2\text{BaNiO}_5$ [13], $\text{Nd}_2\text{BaNiO}_5$ [14], and $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$ [15]. These spin excitations have a purely 1-D dispersion and dynamic structure factor, and are practically indistinguishable from Haldane modes in

Y_2BaNiO_5 , an extensively studied reference Haldane gap system, where no long-range magnetic ordering occurs even at low temperatures [16–19]. The basis of our current understanding of $R_2\text{BaNiO}_5$ compounds is that the Haldane singlet ground state of individual $S = 1$ Ni-chains is preserved in the magnetically ordered phase [13,20]. The non-zero ordered moment on the Ni^{2+} sites is viewed as a result of polarization of the quantum-disordered $S = 1$ chains by an effective staggered exchange field, generated by the ordered R -sublattice.

Based on this physical picture, we shall construct a simple mean-field (MF) model of magnetic ordering in $R_2\text{BaNiO}_5$ materials. In the conventional MF approach all magnetic ions are treated as *isolated* moments that become polarized by the effective exchange field. In the $R_2\text{BaNiO}_5$'s however, in-chain Ni-Ni exchange coupling is dominant over all other magnetic interactions. It is therefore more appropriate to treat only the rare earth ions as individual moments [11]. In the spirit of what is said above, the bare magnetization curve for the Ni-sublattice should be taken in the form of the staggered magnetization function \mathcal{M} for an isolated $S = 1$ quantum spin chain. Ni-Ni interactions are *not* to be included explicitly into the MF theory, since they are already built into the function \mathcal{M} . The MF equations for the Ni-subsystem can thus be written in the following form:

$$M^{(\text{Ni})} = gS\mu_B\mathcal{M}(H^{(\text{Ni})}), \quad (1)$$

$$H^{(\text{Ni})} = 2\alpha_R M^{(R)}. \quad (2)$$

Here $M^{(\text{Ni})}$ and $M^{(R)}$ are the sublattice magnetizations (per ion) for the Ni and R subsystems, respectively, $H^{(\text{Ni})}$ is the effective staggered field that acts on the Ni-chains, $g = 2$ is the gyromagnetic ratio for Ni^{2+} , $S = 1$ is the spin of Ni^{2+} , and α_R is the effective MF coupling constant. To complete the model, we have to write down the MF equations for the R -subsystem as well. Unfortunately, due to the low site-symmetry for R^{3+} ions in $R_2\text{BaNiO}_5$ materials [13], modeling the exact bare magnetization curve of the rare earths is impossible without knowing the details of their electronic structure. Nevertheless, for those compounds in which R^{3+} is a Kramers ion, we can hope to get a reasonable approximation using the Brillouin function:

$$M^{(R)} = M_0^{(R)} \tanh(H^{(R)} M_0^{(R)} / \kappa T), \quad (3)$$

$$H^{(R)} = \alpha_R M^{(\text{Ni})}. \quad (4)$$

Here $M_0^{(R)}$ is the effective moment of the rare earth ion and $H^{(R)}$ is the mean field acting on the rare earths. Direct R - R interactions are expected to be weak, and T_N is predominantly defined by the magnitude of R -Ni exchange. This fact enables us to simplify the equations by omitting R - R coupling in Eq. 4.

Our “semi-quantum” model differs significantly from the usual MF model for classical magnets. In the latter,

at $T \rightarrow 0$ all sublattices become fully saturated as the bare single-ion susceptibility diverges as $1/T$. In contrast, in our model the bare staggered susceptibility of the Haldane chains remains *finite* at $T = 0$. Moreover, at $T \lesssim \Delta$ ($\Delta \approx 9$ meV, or ≈ 105 K $R_2\text{BaNiO}_5$ compounds), the function $\mathcal{M}(H_\pi)$ is expected to be almost T -independent. Our model will therefore produce qualitatively different results for the T -dependencies and saturation values of the magnetic order parameter for Ni.

It has to be noted that the idea of treating interchain coupling at the MF or RPA (Random Phase Approximation) level is, in itself, not a new idea, but a well-established technique [21]. In their pioneering work on CsNiCl_3 , the first Haldane-gap material studied experimentally, Buyers et al. [22], and Affleck [23] implemented this approach to explain magnetic ordering and calculate the spin wave dispersion relations. The main difference between CsNiCl_3 and $R_2\text{BaNiO}_5$ is that exchange coupling between individual Haldane chains is *direct* in the former system, and *mediated by the rare earth ions* in the latter. For directly coupled Haldane spin chains, the magnitude of interchain interactions must exceed some critical value in order for the system to order magnetically [23]. In a MF treatment, the temperature dependence of the ordered moment is defined by the *intrinsic* temperature dependence of the susceptibility of individual chains. In contrast, in our case of $R_2\text{BaNiO}_5$ compounds, magnetic ordering is driven by the $1/T$ -divergent susceptibility of the rare earth subsystem. At sufficiently low temperature long-range order will therefore occur for arbitrary small R -Ni interactions, and in the case of $T_N \lesssim \Delta$, we can use the approximation where the bare magnetization curve of isolated chains is T -independent. $R_2\text{BaNiO}_5$ materials are thus more convenient as model systems for studying the effect of staggered field on Haldane spin chains.

To test the validity of our model we shall compare its predictions for the temperature dependence of sublattice magnetizations with experimental results obtained using neutron diffraction. Since one of our primary goals is to verify that the function \mathcal{M} is indeed T -independent at $T \lesssim \Delta$, we need to compare experimental $M(T)$ curves measured in material with substantially different ordering temperatures. Moreover, as the constant α_R is clearly dependent of R , the only way to exclude T as an implicit variable is to study several dilute systems with the formula $(R_x\text{Y}_{1-x})_2\text{BaNiO}_5$. In such compounds part of the magnetic R^{3+} 's are randomly replaced by non-magnetic Y^{3+} ions. T_N is strongly dependent on the rare earth concentration x [15]. At the same time, we can expect the coupling constant α_R to be the same in all $(R_x\text{Y}_{1-x})_2\text{BaNiO}_5$ systems, provided in Eq. 2 $M^{(R)}$ is replaced by the average moment on the R sites, i.e., by $\bar{M}^{(R)} = xM^{(R)}$. Indeed, in the crystal structure each Ni site is coordinated to four R -sites, and any effect of disorder, for not too small R -content, is reduced by aver-

aging over nearest neighbors, and the effective staggered field scales proportionately to x .

To date, accurate T -dependent data exist only for $\text{Ho}_2\text{BaNiO}_5$ ($T_N = 53$ K) [24] and $\text{Er}_2\text{BaNiO}_5$ ($T_N = 33$ K) [25]. Of these materials only the Er nickelate fits the condition of having a Kramers rare earth ion, essential for using Eq. 3. To have more compounds to work with, and to apply our model to systems with substantially different R -concentrations x , we have performed new powder neutron diffraction studies of $\text{Nd}_2\text{BaNiO}_5$ ($T_N = 48$ K, $x = 1$) and NdYBaNiO_5 ($T_N = 29$ K, $x = 0.5$). The experiments were done on the position sensitive detector diffractometer D1B at the Institut Laue-Langevin, Grenoble, France. Details of the rather straightforward experiment and data analysis will be reported elsewhere. At all temperatures the obtained magnetic structures in both materials are defined by the propagation vector $(1/2, 0, 1/2)$, and are similar to that in $\text{Ho}_2\text{BaNiO}_5$ [24]. In NdYBaNiO_5 the Ni^{2+} and Nd^{3+} moments lie in the (a, c) crystallographic plane, and form almost temperature-independent angles of $\phi^{(\text{Ni})} \approx 35^\circ$ and $\phi^{(\text{Nd})} \approx 0^\circ$ with the c -axis, respectively. The same applies to $\text{Nd}_2\text{BaNiO}_5$ at $T \lesssim 40$ K. Between 40 and 48 K however, i. e., just below T_N , both the Ni and Nd ordered moments in $\text{Nd}_2\text{BaNiO}_5$ undergo a significant re-orientation, in agreement with Ref. [12]. Our principal experimental results, the temperature dependencies of the ordered moments, are summarized in Fig. 1. In the same figure we show the data for $\text{Er}_2\text{BaNiO}_5$, taken from Ref. [25]. In $\text{Er}_2\text{BaNiO}_5$ the orientation of the ordered moments of Ni^{2+} and Er^{3+} is T -independent, with $\phi^{(\text{Ni})} = 65^\circ$ and $\phi^{(\text{Er})} = 88^\circ$, respectively. In the Ho-system the orientation of ordered moments change only slightly with decreasing temperature, and the angles are, correspondingly, $\phi^{(\text{Ni})} \approx 25^\circ$ and $\phi^{(\text{Ho})} \approx 0^\circ$ [24].

We are now in a position to plot $M^{(\text{Ni})}$ as a function of $\tilde{M}^{(R)}$. For $\text{Nd}_2\text{BaNiO}_5$ and NdYBaNiO_5 ($x = 1$ and $x = 0.5$, respectively) this curve is shown in Fig. 2 in solid triangles and squares, correspondingly. For these two materials in which the ordering temperatures differ by almost a factor of 2 we obtain an excellent data collapse, which confirms that the function \mathcal{M} is almost T -independent. To place the $\text{Er}_2\text{BaNiO}_5$ data on the same plot we have to re-scale the absciss to compensate for the difference between α_{Nd} and α_{Er} . This is done in such a way as to obtain the best overlap between the three curves. The best data collapse is achieved by scaling down the Er moment by a factor of 3.2(1) (Fig. 2, open circles). For $\text{Ho}_2\text{BaNiO}_5$, a non-Kramers system, the approximation (3) is not appropriate, yet Eqs. (1,2) are expected to remain valid. We can therefore plot the existing data for $\text{Ho}_2\text{BaNiO}_5$ [24] in the graph on Fig. 2, applying the same absciss-rescaling procedure as for $\text{Er}_2\text{BaNiO}_5$. The best data collapse in this case is obtained by scaling down the Ho moment by a factor 4.2(1) (Fig. 2, open diamonds). We see that, despite the different R -substitute,

the overall shape of the $M^{(\text{Ni})}$ vs. $\tilde{M}^{(R)}$ curve in all four materials is very similar, in support of our conjecture that \mathcal{M} is an intrinsic property of the Ni chains and is the same for all $R_2\text{BaNiO}_5$ systems. For further use we shall fit the cumulative data in Fig. 2 with a purely empirical function:

$$gS\mu_B\mathcal{M}(\alpha_R\tilde{M}^{(R)}) = A \arctan(B_R\tilde{M}^{(R)}), \quad (5)$$

A good fit (solid line in Fig. 2) is obtained with $A = 1.17(4) \mu_B$, $B_{\text{Nd}} = 1.7(1) \mu_B^{-1}$, $B_{\text{Er}} \equiv B_{\text{Nd}}/3.2 = 0.43(3) \mu_B^{-1}$, and $B_{\text{Ho}} \equiv B_{\text{Nd}}/4.2 = 0.33(3) \mu_B^{-1}$.

In the context of our model the curve in Fig. 2 is nothing else but the staggered magnetization function for a Haldane spin chain that we are trying to determine in this study. The only thing we are missing at this point is a proper scale (units of magnetic field) on the absciss, which is currently labeled in units of magnetization. Conversion to field units is done by the coupling constant α , that we shall obtain by analyzing the temperature-dependent experimental data with our mean-field equations. The analysis can be performed for $R = \text{Nd}/\text{Y}$ and $R = \text{Er}$, but not for $R = \text{Ho}$, where, as discussed above, Eq. 3 does not apply. In place of $M_0^{(R)}$ in Eq. 4 we shall use the saturation moment for the rare earth ions in each system. That the values of $M_0^{(\text{Nd})}$ are slightly different in the two Nd-based compounds ($2.68\mu_B$ and $2.3\mu_B$, respectively) only emphasizes the fact that Eq. 4 is no more than an approximation to the actual magnetization function for an isolated R^{3+} ion. Combining our MF equations with Eq. 5 we use least-squares refinement to fit the experimental data in Fig. 1, having α_R as the only adjustable parameter for each compound. Very good fits are obtained for all systems (solid lines in Fig. 1). The only discrepancy is above 40 K for $\text{Nd}_2\text{BaNiO}_5$, where the magnetic structure changes dramatically and our model is not applicable anyway. The refined values for the coupling constants are: $\alpha_{\text{Nd}}^{(1)} = 0.82(2) \cdot 10^5 \text{ Oe}/\mu_B$ in $\text{Nd}_2\text{BaNiO}_5$, $\alpha_{\text{Nd}}^{(2)} = 0.99(2) \cdot 10^5 \text{ Oe}/\mu_B$ in NdYBaNiO_5 , and $\alpha_{\text{Er}} = 0.183(3) \cdot 10^5 \text{ Oe}/\mu_B$ in $\text{Er}_2\text{BaNiO}_5$. Obtaining similar values of α_{Nd} for the two Nd-based nickelates is another self-consistency check for our approach. Equation 2 can now be used to replot the induced moment on the Ni-chains as a function of effective exchange field. As the data collapse in Fig. 2 is rather good, for this purpose we can use the effective average value $\bar{\alpha}_{\text{Nd}} \equiv (\alpha_{\text{Nd}}^{(1)} + \alpha_{\text{Nd}}^{(2)} + 3.2\alpha_{\text{Er}})/3 = 0.8(1) \cdot 10^5 \text{ Oe}/\mu_B$. The resulting staggered field scale is shown in the top axis in Fig. 2.

Our model, simple-minded as it is, appears to adequately describe the magnetic ordering in all $R_2\text{BaNiO}_5$ systems studied so far. Its application provides the first measurement of the staggered magnetization curve for a Haldane spin chain. We have recently succeeded in calculating this function theoretically, extending the approach laid out in Ref. [20]. This calculation is in good agree-

ment with our experimental data, but the discussion is beyond the scope of this paper and will be addressed in a forthcoming publication.

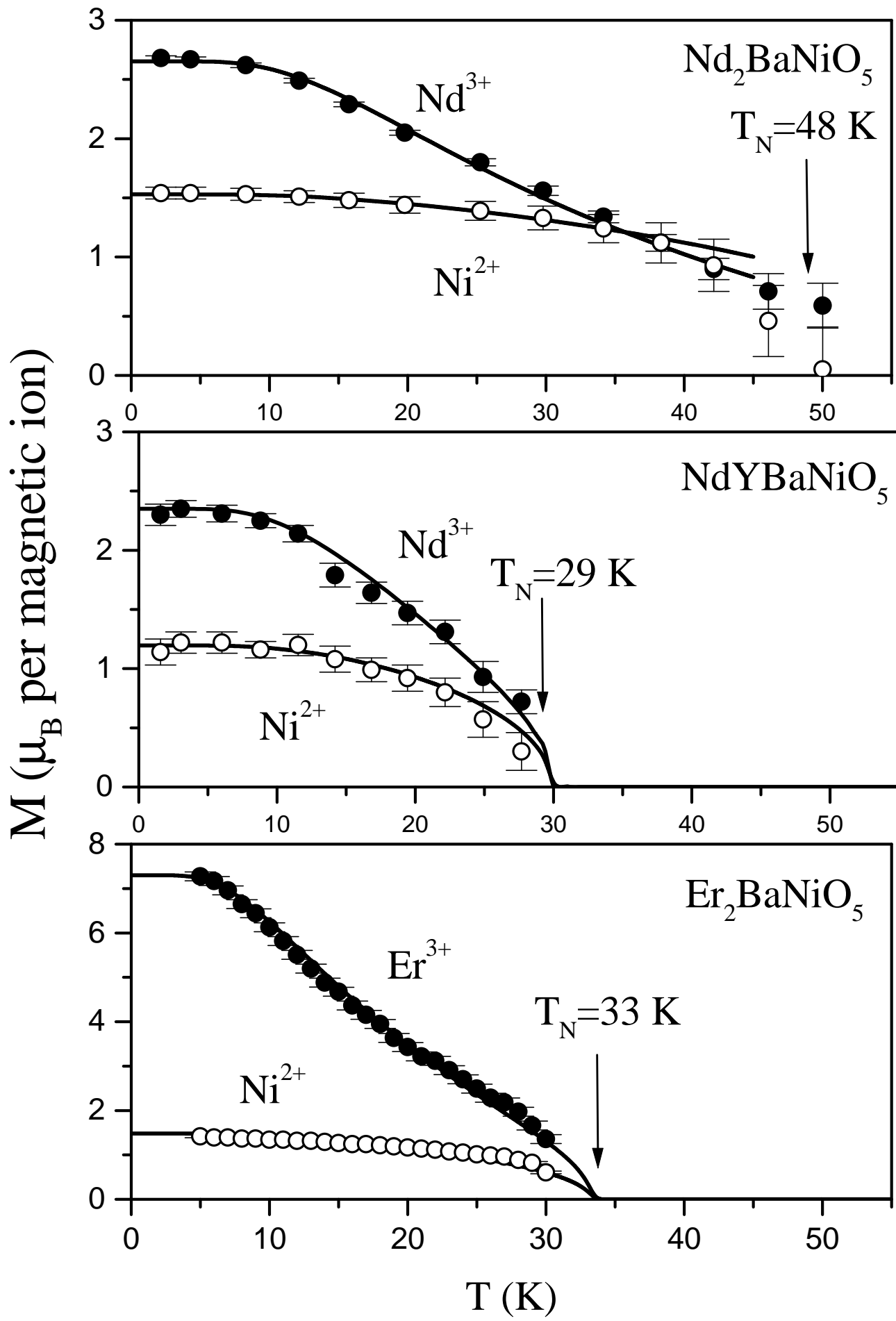
This study was in part supported by the U.S.-Japan Cooperative Program on Neutron Scattering, a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture Japan and The Science Research Fund of Japan Private School Promotion Foundation. Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016, Division of Material Science, U.S. Department of Energy.

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FIG. 1. Measured temperature dependencies of the Ni- (open symbols) and R - (solid symbols) ordered moments in $\text{Nd}_2\text{BaNiO}_5$ and NdYBaNiO_5 (this work), and $\text{Er}_2\text{BaNiO}_5$ (digitized from Ref. [25]). The solid lines are single-parameter fits using the mean field model described in the text.

FIG. 2. Ordered staggered moment on the Ni-chains plotted against the ordered moment of the R -sublattice (bottom axes). The solid line is an empirical fit, as described in the text. The data for $\text{Ho}_2\text{BaNiO}_5$ and $\text{Er}_2\text{BaNiO}_5$ are taken from Refs. [24,25]. The top axis shows the corresponding staggered exchange field acting on the Ni-chains.



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